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ELECTROCHEMICAL DEPOSITION AND CHARACTERIZATION OF DOPED POLY (3,4-ETHYLENE DIOXYTHIOPHENE) FOR POTENTIAL USE AS A BIOSENSOR

Viorel BRÂNZOI[1], **Florina BRÂNZOI**[2], **Alina PRUNĂ**[3],
Nicoleta DONISAN[1]
[1]Dept. of Applied Physical Chemistry and Electrochemistry, University Politehnica of Bucharest, Romania,
[2]Institute of Physical Chemistry, Bucharest, Romania
[3]Dept. of Process Research Nanomaterials, Centro Ricerche Fiat, Orbassano (T0), Italy
email: alinaip@yahoo.com

ABSTRACT

In this study, conducting polymer films of poly(3,4-ethylenedioxythiophene) (PEDOT) were electrodeposited onto a platinum electrode from an aqueous micellar medium. The electroactivity of the undoped and doped PEDOT films were compared. The electrodeposition was characterised by cyclic voltammetry and galvanostatic mode from $LiClO_4$ *solution containing appropriate monomer concentrations and sodium dodecyl sulphate (SDS) as a wetting agent. The resulting polymer films were characterised using cyclic voltammetry in neutral phosphate buffer solutions, SEM and IR spectroscopy.*

KEYWORDS: poly (3,4-ethylene dioxythiophene), doping, cyclic voltammetry, electrochemical polymerization

1. Introduction

Conducting organic polymers and their composites have been studied intensively as electroactive materials in recent years [1]. Poly (3,4-ethylenedioxythiophene) (PEDOT) is one of the most successful polythiophene derivatives due to its interesting properties: high conductivity, unusual electroactivity and a relative environmental stability [2-5].

PEDOT is considered a promising polymer appropriate for continuous sensing and even *in vivo* implantation [6, 7] as it has been proven to own a better aqueous stability and biocompatibility than polypyrrole and polyaniline.

It can be produced either chemically [2], with oxidants like ferric chloride, or electrochemically, in a variety of solvents. The nature of the dopant and the electrolyte would strongly influence the electrochemical and the physical properties of polymers during the polymeric process [8, 9].

Thin PEDOT films are almost transparent and light blue and stable in the oxidized state, and blue in the neutral state. In this study, sodium dodecyl sulphate (SDS) was used as dopant in the synthesis and also as the ionic surfactant.

Our studies revealed that the electrochemically synthesized PEDOT is stable in phosphate buffered solutions, which makes the former polymer an excellent candidate for application in biosensors. This paper reports the detailed results on the electrochemical stability of undoped and SDS-doped PEDOT modified electrodes under physiological conditions by means of cyclic voltammetry measurements, FT-IR spectroscopy, EIS spectroscopy and SEM scanning electron microscopy.

2. Results and experimental research

3,4-Ethylenedioxythiophene (EDOT) was purchased from Aldrich. All other reagents used were of analytical grade and were used as received.

The electrochemical measurements were performed using a Voltalab 40 potentiostat. The electrochemical cell was a conventional three-electrode system with a platinum mesh as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Undoped and doped PEDOT films were synthesized in 0.1 M $LiClO_4$ supporting electrolyte. Various concentrations of SDS were added as dopant to the electrolyte. EDOT polymerization was achieved by both galvanostatic and potentiodynamic deposition methods in absence and presence of the dopant.

Cyclic voltammetry (CV) was used to assess the cycling stability of the undoped and the doped films.

The modified electrodes were subjected to successive cycles CV test, at a scan rate of 25 mVs^{-1}, and the CV curves were measured.

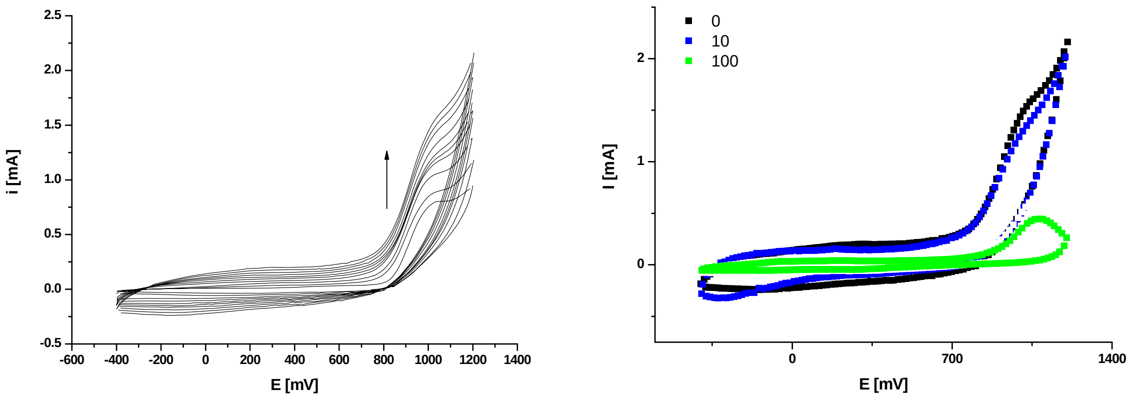
All of the assessment measurements for the obtained films were performed in 0.1M phosphate buffered saline (PBS) solutions (pH 7) and the potentials are given against SCE, unless stated otherwise.

Electrochemical impedance spectroscopy (EIS) was employed to assess the properties of PEDOT films by using the Voltalab 40 equipment.

Morphologies of the polymer-coated electrodes were examined using a Philips SEM-500 scanning electron microscope, at an accelerating voltage of 12 kV, and the formation of PEDOT film was assessed by a Nicolet FT-IR spectrophotometer.

PEDOT films were electropolymerized at the surface of a bare platinum electrode by cyclic voltammetry in the - 0.4 V and 1.2 V potential range. As can clearly be seen in Figure 1, in absence of a dopant, the reaction current increases sharply when the applied potential is larger than 0.7 V, which reveals the formation of the radical cations [10]. The increased current implies that the EDOT radical cations start to electropolymerize onto the platinum electrode.

In the presence of SDS (Figure 1b), it is observed that the current response of doped PEDOT films decreases as the dopant concentration increases. Moreover, the current decreases with continuous cycling in the potential range (Figure 1b). During the first potential scan, the polymerization potential of PEDOT on Pt is around 0.985 V, while the onset of polymerization shifts significantly on the following scans to more positive potentials and stabilizes at 1.080 V, for concentrations above 75 mM SDS.



a) b)

Fig. 1. *The cyclic voltammograms of EDOT polymerization at a scan rate of 20 mVs^{-1} in a) absence of SDS, b) 1st cycle and c) 10th cycle in presence of different SDS concentrations.*

Table 1. *Polymerization potential of SDS-doped PEDOT film as a function of SDS concentration*

[SDS] mM	**Polymerization potential** [mV]
0	818
10	815
25	832
50	865
75	886
100	900

The choice of the electrochemical synthesis method has an influence on the morphology, appearance and adhesion of the polymer [11]. Generally, films obtained by alternating polarization are more adhesive and smoother than the ones obtained at a constant current or potential. As it can be seen in Table 1, when a 0.25 mAcm^{-2} constant current is employed for the electrosynthesis of PEDOT films, the polymerization potential ranges the 0.8-0.9 V potential window and it increases as the SDS concentration value increases. All PEDOT films were smooth and adherent to the surface of Pt electrode. The electrochemical behavior of the PEDOT films deposited electrochemically from aqueous solution, in absence and presence of SDS, was further characterized by using cyclic voltammetry. These films can be cycled repeatedly between the conducting (oxidized) and the insulating (neutral) state, without significant decomposition of the material, which is consistent with the results reported in the literature [12].

The current–voltage characteristic of SDS doped PEDOT films in the potential range of −0.4 to 0.6V in 0.1 M PBS solution (pH 7) is shown in Figure 2. For comparison, the current–voltage wave of undoped PEDOT polymerized in 0.1 M LiClO$_4$ electrolyte is also displayed. As can be seen, the curves of these polymer films have a nearly rectangular shape, which is typical of the pure capacitive behavior of the tested object [13]. However, the current of film obtained by potentiodynamic method in presence of 75 mM dopant is nearly 3 times that of the film gained in absence of the dopant, which proves that more SDS can hinder the polymer electroactivity after a certain concentration. The same observation can be made for the case of galvanostatic synthesis, the decrease of film current being more evident as the SDS concentration increases.

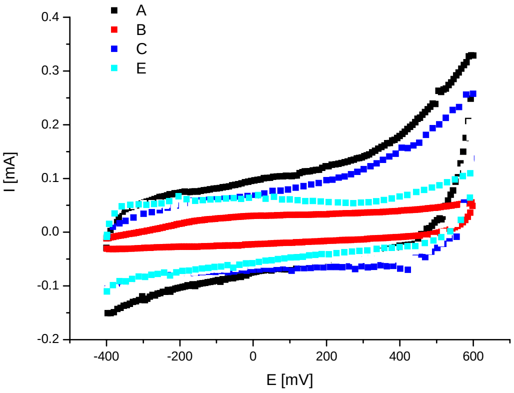


Fig. 2. *Voltammetric behavior of the PEDOT/SDS/Pt electrode in comparison with the PEDOT/Pt electrode obtained by potentiodynamic mode: A – in absence of SDS, B – in presence of 75 mM SDS and galvanostatic electrodeposition mode in presence of: C – 10 mM SDS, D – 100 mM SDS in 0.1M LiClO$_4$ electrolyte at 25 mVs^{-1}*

Electrochemical impedance spectrometry is a more reliable technique than cyclic voltammetry for measuring the capacitance with minimised effect from non-capacitive Faradaic contributions [14]. Therefore, the doped and pure polymer films were studied by EIS. The resulting Nyquist plots for PEDOT and SDS-doped PEDOT systems obtained by galvanostatic and potentiodynamic modes are shown in Figures 3 and 4. As can be observed in Figure 3, the Nyquist plot for PEDOT film is featured by a vertical trend at low frequencies, indicating a capacitive behaviour according to the equivalent circuit theory. When SDS was added to the polymer, the capacitive behaviour could be observed to be replaced by the more inclined diffusion line as the SDS concentration increased. It can be said that increasing SDS concentration leads to an increasing diffusive behaviour, observation corroborated with the changed morphology of doped PEDOT film in Figure 5c.

The capacitances of the electrode materials were calculated according to the equation: $C = -1/(2\pi f Z_{im}$ (f = frequency; Z_{im} = imaginary impedance), from the slope of the linear correlation between the imaginary impedance and the reciprocal of the frequency at low frequencies (see Figure 4c). One can observe the decrease of capacitance value for SDS-doped PEDOT films as compared with undoped ones: it is smaller as the SDS concentration increases (see Table 2). The SDS leads to increased capacitance value but only if added up to 10 mM concentration to the polymerization electrolyte.

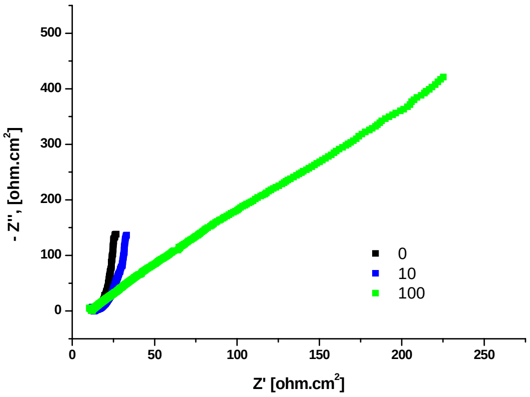


Fig. 3. *Nyquist plots for PEDOT and SDS-doped PEDOT films obtained by galvanostatic deposition at open circuit potential in 0.1M PBS solution, as a function of SDS concentration.*

Table 2. *Capacitance values of undoped and SDS-doped PEDOT films (obtained galvanostatically) at 0.01Hz, as a function of SDS concentration*

[SDS] **mM**	**Slope values obtained from graph** **$-Z_{im} = f(1/2\pi f)$**	**C** [F/cm^2]
0	161.1	0.0062
10	160.81	0.0063
75	365	0.0027
100	294.33	0.0034

The real impedance at low frequencies, where the capacitive behaviour dominates, is an indication of the combined resistance of the electrolyte and the film including both electronic and ionic contributions. It can be seen that the undoped PEDOT films (the ones doped with a low concentration of SDS, 10mM) were significantly lower in resistance than the other SDS-doped PEDOT films. It has been already mentioned that, in general, the real impedance of an electrode material also decreases as the material’s porosity increases, due to an improved ionic accessibility [15].

This is in agreement with the SEM results presented below that suggest a much higher porosity in the SDS-doped PEDOT films than in the undoped polymer counterparts. Further, the Nyquist plots of potentiodynamically obtained undoped and SDS-doped PEDOT are displayed in Figure 4.

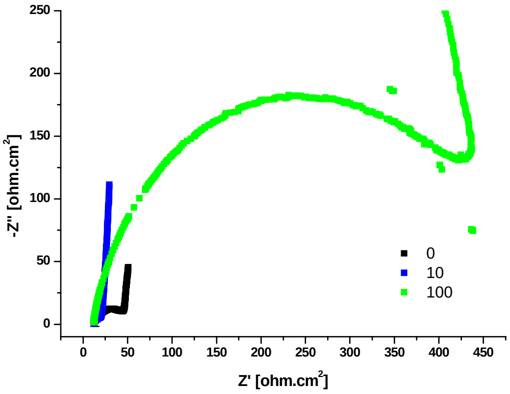
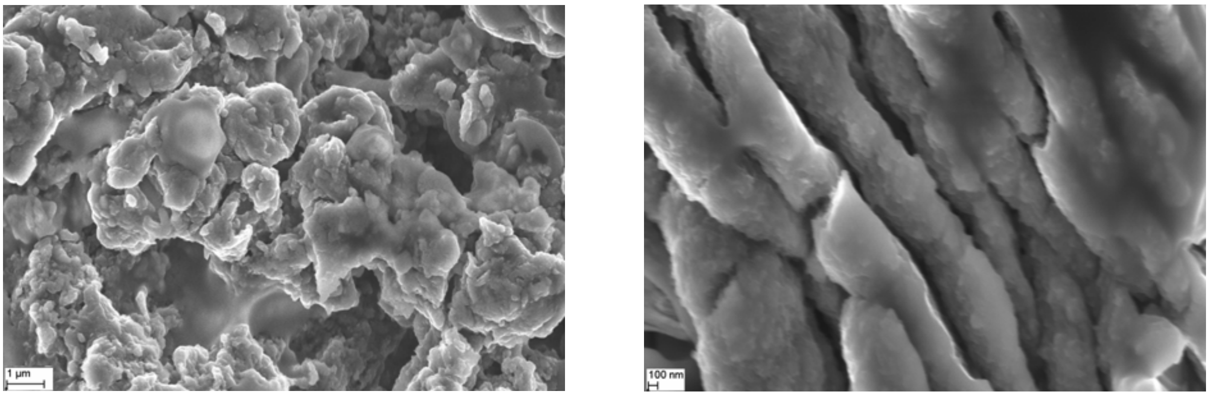


Fig. 4. *Nyquist plots for PEDOT and SDS-doped PEDOT films obtained by potentiodynamic deposition at open circuit potential in 0.1M PBS solutions, as a function of SDS concentration.*

The impedance plot is composed of a semicircle at high frequencies and a capacitive slope at low and middle frequencies. The semicircle that appears at high frequencies is considered to be an effect of the charge transfer resistance originating in the interface structure between the porous electrode surface and the electrolyte [10]. At low frequencies, the impedance plot becomes a near vertical line. A capacitive behaviour is observed when SDS in a concentration up to 10 mM is added, as depicted in Figure 4.

In both cases of galvanostatic and potentiodynamic depositions, undoped PEDOT showed a porous morphology with a large surface area, making it a suitable matrix for immobilizing enzymes to its surface. Figure 5 shows the SEM images of the PEDOT film: in Figure 5a a nodular accumulating structure is highlighted (the size of the nodules start from a few hundred nanometers in diameter and they aggregate to form gobbets); in Figure 5b, the effect of high concentration of SDS on the morphology of the PEDOT film can be observed: lamellar structure with almost vertical orientation to the substrate.

It is evident that SDS dopant changes the morphology of the PEDOT film into a more porous structure with a higher interface area.



a) b)

Fig. 5. *SEM images of a) the film surface of undoped PEDOT synthesized by potentiodynamic deposition and b) galvanostatically obtained PEDOT, doped with 75 mM SDS.*

FT-IR studies showed that the polymer was formed after only 5 min of polymerization. The spectrum shows several bands out of which the band at 819 cm^{-1} is assigned to the symmetric C-S-C deformation [17], and the band at 1053.91 cm^{-1} is assigned to the symmetric C-O-C ether bond. Thereafter no major changes were observed. It can be noted that the signal at 800 cm^{-1} disappeared and signals at 1640 cm^{-1} and in the 3000–4000 cm^{-1} region appear. The first signal can be assigned to an aromatic CH out-of-plane swing vibration of the terminal thiophene group [18], which will decrease as the reaction proceeds.

3. Conclusion

Pure and SDS-doped PEDOT films were electrodeposited galvanostatically and potentiodynamically on a Pt surface. The current response of doped PEDOT films decreased as SDS concentration increased, the value of 10 mM SDS being the one at which the SDS-PEDOT system seems deteriorated. The effect of the SDS surfactant on the electrochemical properties of the doped PEDOT could be supported by the CV, EIS and SEM results. A more porous and lamellar structure was obtained when adding more SDS in a concentration higher than 10 mM. Nearly rectangular shaped CV^s are obtained for all films suggesting that the charge and the discharge reversibly occur at the electrode/electrolyte interface. Higher capacitance values were exhibited by pure PEDOT and PEDOT doped films, with 10 mM SDS. The results obtained can be used to get the desired value of the capacitance by choosing the adequate preparation method and by controlling the microstructure of the composites.

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